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(54) Title: EMULSIFIED WATER BLENDED FUELS PRODUCED BY USING A LOW ENERGY PROCESS AND NOVEL SURFACTANT

(57) Abstract: A novel low energy process to produce water in oil emulsions in particular water blended fuels by employing a low molecular weight surfactant with an emulsifier package.

TITLE: EMULSIFIED WATER BLENDED FUELS PRODUCED BY USING
A LOW ENERGY PROCESS AND NOVEL SURFUCTANT

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Field of Invention

The invention relates to a novel low energy process to produce a water in oil emulsion, in particular water blended fuels with good emulsion stability. More particularly, the invention relates to the use of a low molecular weight surfactant to make a water in oil emulsion by a low energy, low shear process.

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Background of the Invention

Internal combustion engines, especially diesel engines, using water fuel blends results in the combustion chamber producing lower nitrogen oxides (NO_x), hydrocarbons and particulate matter emissions. NO_x emissions have become an important environmental issue because it contributes to smog and air pollution. Governmental regulations and environmental concerns have driven the need to reduce NO_x emissions from engines. In particular, the U.S. Clean Air Act will require about 90% to 95% reduction of the current level of internal combustion engines emissions by the year 2007. Similar regulations are expected in Europe and other parts of the industrialized world.

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Diesel fueled engines produce NO_x due to the relatively high flame temperatures reached during combustion. The reduction of NO_x production conventionally includes the use of catalytic converters, using "clean" fuels, recirculation of exhaust and engine timing changes. These methods are typically expensive or complicated to be readily commercially available.

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Water is inert toward combustion, but lowers the peak combustion temperature resulting in reduced particulates and NO_x formation. When water is added to the fuel it forms an emulsion and these emulsions are generally unstable. Stable water in fuel emulsions of a small particle size are difficult to reach and maintain.

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The use of emulsified fuels to reduce emissions have been disclosed in other patents and patent applications of Applicant, such as USPN 6,280,485, 6,383,237, 6,368,367, 6,368,366 and 6,280,485 and USSN 09/761,482 all incorporated herein by reference and assigned to the assignee
5 of the present application. Emulsified fuels have been made by high energy intensive processes. It would be advantageous to develop a low energy process to make stable water in fuel emulsions.

The present invention has discovered the use of certain low molecular weight surfactants that lower interfacial tension at the water oil
10 interface resulting in a low energy process to make a water in oil emulsion fuels.

The term "NO_x" is used herein to refer to any of the nitrogen oxides, NO, NO₂, N₂O, or mixtures of two or more thereof. The terms "water-in-oil" emulsion, "water emulsion", "emulsions", "water blended fuel", "emulsified
15 water fuel" and other variations are interchangeable.

Summary of the Invention

The invention relates to an emulsified water in oil composition comprising:

- A. a fuel in the range of about 50% to about 99% by weight of the composition;
- 20 B. a water in the range of about 1% to about 50% by weight of the composition;
- C. an emulsifier in the range of about 1% to about 50% by weight of the composition;
- D. a low molecular weight surfactant in the range of about 0.001%
25 to about 15% by weight of the composition wherein the surfactant comprises:
 - i) natural fats;
 - ii) non-ionic and ionic surfactants;
 - iii) co-surfactants;
 - iv) fatty acids and their amine salts; or
 - 30 v) combinations thereof; and
- E. optionally ammonium nitrate.

The surfactant lowers the interfacial tension of the water in oil interface during emulsion and formation and is a low molecular weight surfactant that is less than or equal to 950 g/mol.

Further, the invention relates to a low energy process for making a water in oil emulsion comprising emulsifying a fuel, a water, an emulsifier, and a low molecular weight surfactant. The water in oil emulsion is produced utilizing a low energy processing technology using low shear rates and does not need to employ high shear rates.

The invention further relates to a low energy process to produce an emulsified water in oil composition from a concentrate comprising emulsifying a portion of a fuel, a portion to substantially all of a water depending on whether it is an emulsified concentrate or an additive concentrate, substantially all of an emulsifier, substantially all of a low molecular weight surfactant to form a concentrate emulsion; and then diluting the concentrated emulsion with the remaining portion of fuel and water at the time of use.

The water in oil emulsion provides good emulsion stability. The water in oil composition is useful as a fuel for stationary and/or combustion engines and/or open flame burning apparatus.

Detailed Description

The invention discloses a stable emulsified water in oil composition made by a low energy process by low shearing the emulsion. The emulsified water in oil composition employs a low molecular weight surfactant so that a low shear rate mixing condition can be used to make the emulsion.

Surfactant

The surfactant is a small surfactant, having a molecular weight (Mw) of about less than or equal to about 950 g/mol, in another embodiment about 900 g/mol to about 30 g/mol, in another embodiment about 400 g/mol to about 90 g/mol, and in another embodiment about 350 g/mol to about 150 g/mol. Further the low molecular weight surfactant has properties to lower the interfacial tension at the water/oil interface during emulsion formation. The low molecular weight surfactant further orients itself to the water/oil interface quickly by populating the water oil interface. The use of the low molecular

weight surfactant results in a low energy process to make the water in oil emulsion, in particular an emulsified water fuel.

The surfactant includes but is not limited to a) natural fats; b) non-ionics surfactants; c) co-surfactants; d) fatty acids and their amine salts; and
5 e) combinations thereof. The surfactant is in the range of about 0.001% to about 15%, in another embodiment about 0.01% to about 10%, in another embodiment about 0.05% to about 5%, and in another embodiment about 0.1% to about 3% by weight of the water in oil composition. The surfactants can be used alone or in combination. In one embodiment the preferred
10 surfactant is a natural fat surfactant.

The natural fat surfactants include but are not limited to triglycerides, hydrolyzed triglycerides, oxidized products of triglycerides, vegetable oils, refined vegetable oils, used vegetable oils and the like. The preferred natural fat surfactant is a refined used vegetable oil. The natural
15 fats can be used alone or in combination.

The non ionic and ionic surfactants include but are not limited to alkyl ethoxylates, ethoxylated alkylphenols, alkyl glucosides, ethoxylated alcohols, ethoxylated amines, amides derived from fatty acids and/or alcohols, ethers or fatty alcohols, esters of fatty acids and the like. In addition the non-
20 ionic and ionic surfactants have a hydrophilic lipophilic balance (HLB) in the range of about 2 to about 40, in one embodiment, about 2 to about 10, in one embodiment about 10 to about 15 and in another embodiment about 4 to about 8. Examples of these non-ionic and ionic surfactants are disclosed in
25 *McCutcheon's Emulsifiers and Detergents*, 1993, North American & International Edition. Some examples include but are not limited to alkanolamides, alkylarylsulfonates, amine oxides, poly(oxyalkylene) compounds, including block copolymers comprising alkylene oxide repeat units (e.g., Pluronic™ s), carboxylated alcohol ethoxylates, ethoxylated alcohols, ethoxylated alkyl phenols, ethoxylated amines and amides,
30 ethoxylated fatty acids, ethoxylated fatty esters and oils, fatty esters, glycerol esters, glycol esters, imidazoline derivatives, lecithin and derivatives, lignin and derivatives, monoglycerides, diglycerides and derivatives, phosphate

esters and derivatives, propoxylated and ethoxylated fatty acids or alcohols or alkyl phenols, sorbitan derivatives, sucrose esters and derivatives, sulfates or alcohols or ethoxylated alcohols, sulfonates of dodecyl and tridecyl benzenes or condensed naphthalenes or petroleum and the like. Preferably the non
5 ionic surfactants are Neodol 25-3, C12 – C 14 alcohol with two ethoxylates and Ethomeen C12. The non ionic and ionic surfactants may be used alone or in combination.

Additionally, the ethoxylated alcohols include but are not limited to oleyl alcohol with 5 ethoxylates, Tomadol 91-8 (purchased from Tomah Chemical)
10 and the like. The ethoxylated alcohol contains about 5 to about 24, preferably about 8 to about 20 and more preferably about 5 to about 12 carbon atoms with about 3 to about 30 preferably about 5 to about 25 and more preferably about 5 to about 10 ethylene oxide groups. Preferably the ethoxylated alcohol is oleyl alcohol with 5 ethoxylates. The ethoxylated alcohols may be used
15 alone or in combination.

Another example of non-ionic and ionic surfactants include but are not limited to IGEPAL CO-630, (nonylphenoxypoly(ethyleneoxy) ethanol; nonoxynol-8), IGEPAL CO-430, IGEPAL CO 530, available from Rhone-Poulenc, Cranbury, New Jersey, USA; TERGITOL® NP-9 (a-(4-nonylphenyl)-
20 ∞ -hydroxypoly(oxy-1,2-ethanediyl)), available from Union Carbide Corporation, Danbury, Connecticut, USA); and alcohol ethoxylates available from Tomah Products, Inc. under the name "Tomadol"™ alcohol ethoxylates and the like.

In another embodiment the non-ionic and ionic surfactants include but are not limited to sorbitan esters of fatty acids, sorbitan monooleate (SMO);
25 sorbitan monoisostearate (SMIS); glycerol esters like glycerol monooleate (GMO); glycerol dioleate; and mono-unsaturated acids such as oleic and elaidic acid; poly-unsaturated acids such as linoleic and linolenic acid; 1,6-dilauryl diglycerol; monooleyl diglycerol; mono cetyl ether of glycerol; mono oleyl glycerol; diethylene glycol mono-stearate; and the like. In one
30 embodiment the preferred non-ionic surfactants are glycerol monooleate, sorbitan monooleate and combinations thereof.

In another embodiment the non-ionic and ionic surfactants include but are not limited to esters of the fatty acids include but are not limited to glyceryl mono-oleate, glyceryl monostearate, glyceryl monoricinoleate, pentaerythritol monolaurate, pentaerythritol mono and dioleate, pentaerythritol
5 monocaprylate, mono, di, and triethylene glycol mono-oleate, propylene glycol monoricinoleate; monoethylene glycol mono-oleate, triethylene glycol monostearate, sorbitol monolaurate, mannitol mono-oleate, mannitol dioleate, sorbitol, dioleate, sorbitan dioleate, sorbitan mono and dilaurate, mannitan mono and distearate, mannitan mono and dioleate, sorbitan mono and
10 dipalmitate, sorbitan sesquioleate, mannitan monolaurate, and the like.

Partial esters obtained from polyhydric alcohols are useful as the surfactant include but are not limited to the cyclic ether-alcohol esters which have been modified by being further reaction with an alkylene oxide or a polyalkylene oxide. For example, a sorbitan mono-oleate may be further
15 modified by treatment with ethylene oxide to form the hydroxyl ether or sorbitan mono-oleate. Other modified esters of this type may be the polyoxyalkylene sorbitan monostearate, polyoxyalkylene sorbitan mono-oleate, polyoxyalkylene sorbitan monolaurate, polyoxyalkylene sorbitan di and tri-oleate, oleic ester of polyoxyalkylene mannitol, and the like. In another
20 embodiment the non-ionic surfactants include but are not limited to the etherification of the cyclic ether-alcohols of fatty acids containing 12 or more carbon atoms and may be derived from natural fats and oils or pure fatty acids or their mixtures may be used. The free fatty acids may be exemplified by capric, palmitic, oleic, stearic acid or the like. In addition to the fatty acids
25 other acids may be used and may be exemplified by naphthenic, sulfonic, salicylic acids and the like.

In another embodiment the non-ionic and ionic surfactants include but are not limited to fatty acid alkanol amides such as available from Witco Corporation under the name SCHERCOMID™, SCHERCOMID™SO-A and
30 Oleamide DEA, lauric acid, myristic acid, coconut acid, coconut oil, oleic acid, tall oil fatty acid, linoleic acid, soybean oil, apricot kernel oil, wheat germ oil, monocarboxylic fatty acids, triglycerides, and mixtures thereof.

The co-surfactant has sufficient polar groups to render the co-surfactant partially soluble in both phases. The co-surfactants include but are not limited to alcohols, amines, amides, esters, ketones, ethers and mixtures thereof. The co-surfactant has at least 1 to about 24, in another embodiment about 1 to about 10, in another embodiment about 1 to about 8 carbon atoms. The co-surfactants may be used alone or in combination.

The alcohol co-surfactant has about 1 to about 6, in another embodiment about 1 to about 4 and in another embodiment 1 to 3 hydroxy groups in the molecule. Such alcohols may be aliphatic, saturated or unsaturated, and straight chain or branched or cyclic derivatives thereof. Saturated, aliphatic, straight chain alcohols are preferred. The alcohol surfactants include but are not limited to propylene glycol, ethylene glycol, isopropanol, 2 ethyl hexanol, stearyl alcohol, oleyl alcohol, methanol, ethanol and the like. The preferred alcohol surfactant is propylene glycol. The alcohols may be used alone or in combinations.

The fatty acids and their amine salts include but are not limited to N,N-diethyl ethanolamine salts of oleic acid, tall oil fatty acids, stearic acid, palmitic acid, lauric acid and the like. The preferable fatty acid and their amine salt is oleic acid-diethyl ethanol amine salt. The fatty acids and their amine salts can be used alone or in combination.

The water in oil emulsion is comprised of a continuous fuel-phase, a discontinuous water or aqueous phase, an emulsifying amount of emulsifier and a low molecular weight surfactant so that the process does not require high speed shear to emulsify the fuel and water.

In the practice of the present invention the water in oil emulsion is made by a batch, semi-batch or a continuous process. A concentrate may be made and used. The process is capable of monitoring and adjusting the flow rates of the fuel, emulsifier, surfactant, additives and/or water to form a stable emulsion with the desired water droplet size. The water phase of the emulsified fuel is comprised of droplets having a mean diameter of about 1.0 microns or less, in another embodiment about 0.8 microns or less, in another embodiment about 0.5 microns or less, in another embodiment about 0.15

microns or more, in another embodiment about 1.0 micron to about 0.5 microns, and in another embodiment about 1.0 micron to about 0.2 microns.

The emulsified fuel may be prepared by the steps of mixing the fuel, the emulsifier, the low molecular weight surfactant, and other oil soluble
5 additive using low shear techniques to form the fuel additive mixture. Then the fuel additive mixture is mixed with water and optionally any desired water soluble additives to form the desired emulsified water blended fuel.

In a batch process the water, the emulsifier, the surfactant, the fuel and optional additives are added to a tank, in the desired amounts. The mixture is
10 emulsified using an emulsification device in the vessel, or alternatively the mixture flows from the vessel via a circular line to the emulsification device which is external to the vessel, for about 1 to about 20 tank turnovers. The temperature in the range of about ambient temperature to about 212°F, and in another embodiment in the range of about 40°F to about 150°F, and at a
15 pressure in the range of about atmospheric pressure to about 10 atmospheres, in another embodiment about atmospheric pressure to about 80 psi, in another embodiment in the range of about 15 psi to about 30 psi.

The continuous process described herein depicts another embodiment of the invention. The feeds of the fuel, emulsifier, surfactant, water and
20 optional additives are introduced as discrete feeds or in the alternative combinations of the discreet feeds. The processing streams are introduced in or as close to the inlet of the emulsification device as possible. It is preferable that the emulsifier is added to the fuel as a fuel emulsifier stream prior to the discreet feeds combining together. The continuous process generally occurs
25 under ambient conditions. The continuous process is generally done at atmospheric pressure to about 500 psi, in another embodiment in the range of about atmospheric pressure to about 120 psi, and in another embodiment in the range of about atmospheric pressure to about 50 psi. The continuous process generally occurs at ambient temperature. In one embodiment the
30 temperature is in the range of about ambient temperature to about 212°F, and in another embodiment in the range of about 40°F to about 150°F.

Alternatively, a concentrate is formed and all or substantially all the water, and water soluble additive and a portion of the fuel and all or substantially all the emulsifier and low molecular weight surfactant is emulsified under low shear conditions to form a concentrate fuel. The emulsified fuel, when used, is then blended under normal mixing conditions with the remaining portion of the fuel so that high speed emulsification conditions are not necessary.

The process may be in the form of a containerized equipment unit that operates automatically. The process can be programmed and monitored locally at the site of its installation, or it can be programmed and monitored from a location remote from the site of its installation. The fully formulated water fuel blend is optionally dispensed to end users at the installation site, or in another embodiment end users can blend the concentrated emulsion with the final portion of fuel. This provides a way to make the water in fuel emulsions available to end users in wide distribution networks.

The emulsification may occur at high shear conditions that are greater than $50,000 \text{ s}^{-1}$. However, the composition is emulsified at low shear process conditions. The emulsification provides for the desired particle size and a uniform dispersion of water in the fuel and occurs at a shear rate in the range of less than or equal to $50,000 \text{ s}^{-1}$, and in another embodiment about $50,000 \text{ s}^{-1}$ to about $20,000 \text{ s}^{-1}$, and in another embodiment of about $20,000 \text{ s}^{-1}$ to about $1,000 \text{ s}^{-1}$, and in another embodiment less than $1,000 \text{ s}^{-1}$ to about 1 s^{-1} , and in another embodiment less than 100 s^{-1} to about less than 1 s^{-1} and in another embodiment less than 10 s^{-1} to about less than 1 s^{-1} shearing. If more than one emulsification step is used, the shear rates of the emulsification steps can be the same, similar or different, depending on the emulsifier and low molecular weight surfactant used.

The emulsification occurs by any low shear method used in the industry including but not limited to mixing, mechanical mixer agitation, static mixers, centrifugal pumps, positive displacement pumps, orifice plates, and the like. Examples of the devices include but are not limited to an Aquashear, pipeline static mixers, rotor/stator mixers and the like. The Aquashear is a

low-pressure hydraulic shear device. The Aquashear mixers are available from Flow Process Technologies Inc.

The emulsification is able to occur at a low shear rate and does not require a high shear rate. By using a low shear rate, low energy process to
5 make a stable and good emulsified water in oil blend/fuel one uses less complex or simpler technology, equipment, devices and is more cost and/or time efficient.

Example 1

About 0.3 parts by weight of glycerol monooleate and about 2.3 parts
10 by weight of a concentrate mixture containing about 23% wt 2300 MW PIB succinic acid/diethyl ethanolamine salt plus about 31% wt oleic acid/diethyl ethanol amine salt plus about 9.7% of about a 50% ammonium nitrate solution and about 4.7% propylene glycol is mixed into about 77.0 parts by weight of diesel fuel. This organic mixture is then co-fed with about 20 parts by weight
15 water through an 8.0 mm diameter Sulzer SMX static mixer unit consisting of about 48 mixing elements at a total volumetric flow rate of about 470 millilitres per minute. The final white emulsion was placed in storage bottles. After standing for one month at room temperature, about 99% of the material was still an emulsion. No banding or water was observed and only about 1% of
20 the diesel fuel had separated. Particle size, oil separation, and sedimentation were found to be comparable to emulsifiers made using high shear mixing. The particle size of the emulsion was found to have a mean volume diameter of less than about 1 micron. The storage bottles were stored at room temperature and observed at various time intervals. It was observed that the
25 emulsion exhibited stability behavior equivalent to emulsions made using high shear conditions, i.e. about 3 part by volume (pbv) of banded material at the bottom of the storage bottle after 7 days and about 7 pbv after 28 days. In addition no free water was observed.

Fuel

30 The fuel comprises hydrocarbonaceous petroleum distillate fuel, non-hydrocarbonaceous materials that include but are not limited to water, oils, liquid fuels derived from vegetable sources, liquid fuels derived from minerals

and mixtures thereof. Suitable fuels include, but are not limited to, gasoline, diesel, kerosene, naphtha, aliphatics and paraffin. The fuel comprises non-hydrocarbonaceous materials include but is not limited to alcohols such as methanol, ethanol and the like, ethers such as diethyl ether, methyl ethyl ether
5 and the like, organo-nitro compounds and the like; fuels derived from vegetable or mineral sources such as corn, alfalfa, shale, coal and the like. The fuel also includes but is not limited to gas to liquid fuels. The fuel also includes but is not limited to mixtures of one or more hydrocarbonaceous fuels and one or more non-hydrocarbonaceous materials. Examples of such
10 mixtures are combinations of gasoline and ethanol and of diesel fuel and ether and the like.

In one embodiment, the fuel is any gasoline. Including, but not limited to a chlorine-free gasoline or a low-chlorine gasoline, or a low sulfur gasoline or sulfur-free gasoline and the like.

15 In one embodiment, the fuel is any diesel fuel. The diesel fuels include, but are not limited to, those that contain alcohols and esters, has a sulfur content of up to about 0.05% by weight or sulfur-free, is a chlorine-free or low-chlorine diesel fuel and the like.

The fuel is present in the emulsified fuel at a concentration of about
20 50% to about 95% by weight, and in one embodiment about 60% to about 95% by weight, and in one embodiment about 65% to about 85% by weight, and in one embodiment about 80% to about 90% by weight of the emulsified fuel.

Water

25 The water used in the emulsified fuel may be taken from any source. The water includes but is not limited to tap, deionized, demineralized, purified, for example, using reverse osmosis or distillation, and the like. The water includes water mixtures that further includes but are not limited to antifreeze components such as alcohols and glycols, ammonium salts such as
30 ammonium nitrate, ammonium maleate, ammonium acetate and the like, and combinations thereof; and other water soluble additives.

The water is present in the emulsified fuel at a concentration of about 1% to about 50% by weight, in one embodiment about 5% to about 40% by weight, in one embodiment about 5% to about 25% by weight, and in one embodiment about 10% to about 20% by weight of the emulsified fuel.

- 5 In another embodiment the water is present in the emulsified fuel at a concentration of less than 1% by weight, in another embodiment less than 0.5% by weight, in another embodiment less than 0.1% by weight, and in another embodiment in the range of about 0.1% to about 1% by weight of the emulsified fuel. An emulsified water in oil composition can be made with
10 water at these low levels with the fuel, the emulsifier, the surfactant and optionally ammonium nitrate and in another embodiment without the surfactant and with the fuel, the emulsifier and optionally the ammonium nitrate.

Emulsifier

- 15 The emulsifier includes but is not limited to
- (i) at least one fuel-soluble product made by reacting at least one hydrocarbyl-substituted carboxylic acid acylating agent with ammonia or an amine including but not limited to alkanol amine, hydroxy amine, and the like, the hydrocarbyl substituent of said acylating agent having about 50 to about
20 500 carbon atoms;
 - (ii) a second acylating agent having at least one hydrocarbyl substituents of up to about 40 carbon atoms, and reacting that said acylating agent with ammonia or an amine;
 - (iii) at least one of an ionic or a nonionic compound having a
25 hydrophilic-lipophilic balance (HLB) of about 1 to about 40;
 - (iv) mixture of (ii) or (iii) with (i) or a mixture of (i), (ii), and (iii);
 - (v) a water-soluble compound selected from the group consisting of amine salts, ammonium salts, azide compounds, nitrate esters, nitramine, nitrocompounds, alkali metal salts, alkaline earth metal salts, in combination
30 with (i), (ii), (iii), (v), (vii) or combinations thereof;
 - (vi) the reaction product of polyacidic polymer with at least one fuel soluble product made by reacting at least one hydrocarbyl-substituted

carboxylic acid acylating agent with ammonia, an amine, a polyamine, an alkanol amine or hydroxy amines;

(vii) an amino alkylphenol which is made by reacting an alkylphenol, an aldehyde and an amine resulting in an amino alkylphenol;

5 (viii) a nitrogen free emulsifier; or

(ix) the combination of (i) through (viii) or combinations thereof.

The emulsifier has at least one high molecular weight component. The emulsifier has a high molecular weight component relative to the surfactant which has a low molecular weight.

10 The fuel-soluble product (i) of the emulsifier may be at least one fuel-soluble product made by reacting at least one hydrocarbyl-substituted carboxylic acid acylating agent with ammonia or an amine including but not limited to alkanol amines, hydroxy amines, and the like, the hydrocarbyl substituent of said acylating agent having about 50 to about 500 carbon
15 atoms, and is described in greater detail in USSN 09/761,482, An Emulsifier For An Aqueous Hydrocarbon Fuel, incorporated by reference herein.

The hydrocarbyl-substituted carboxylic acid acylating agents may be carboxylic acids or reactive equivalents of such acids. The reactive equivalents may be acid halides, anhydrides, or esters, including partial esters
20 and the like. The hydrocarbyl substituents for these carboxylic acid acylating agents may contain from about 50 to about 500 carbon atoms, and in one embodiment about 50 to about 300 carbon atoms, and in one embodiment about 60 to about 200 carbon atoms. In one embodiment, the hydrocarbyl substituents of these acylating agents have number average molecular
25 weights of about 700 to about 3000, and in one embodiment about 900 to about 2300.

In another embodiment, the fuel soluble product (i) of the present invention comprises an emulsifying amount of at least one of a fuel-soluble hydrocarbyl-substituted carboxylic acylating agent and a reaction product of
30 said acylating agent with at least one of ammonia, an amine, an alcohol, a reactive metal, a reactive metal compound or a mixture of two or more

thereof, wherein the hydrocarbyl substituent comprises a group derived from at least one polyolefin, said polyolefin having $\overline{M}_w/\overline{M}_n$ greater than about 5.

The hydrocarbyl substituted acylating agents have a hydrocarbyl group substituent that is derived from a polyolefin, with polydispersity and other
5 features as described below. Generally, it has a number average molecular weight of at least 600, 700, or 800, to 5000 or more, often up to 3000, 2500, 1600, 1300, or 1200. Typically, less than 5% by weight of the polyolefin molecules have \overline{M}_n less than about 250, more often the polyolefin has \overline{M}_n of at least about 800. The polyolefin preferably contains at least about 30%
10 terminal vinylidene groups, more often at least about 60% and more preferably at least about 75% or about 85% terminal vinylidene groups. The polyolefin has polydispersity, $\overline{M}_w/\overline{M}_n$, greater than about 5, more often from about 6 to about 20. The hydrocarbyl group is typically derived from a polyolefin or a polymerizable derivative thereof, including homopolymers and
15 interpolymers of olefin monomers having 2 to 30, to 6, or to 4 carbon atoms, and mixtures thereof. In a preferred embodiment the polyolefin is polyisobutenyl.

Suitable olefin polymer hydrocarbyl groups, having suitable polydispersity, can be prepared by heteropolyacid catalyzed polymerization of
20 olefins under conventional conditions. Preferred heteropolyacids include a phosphotungstic acid, a phosphomolybdic acid, a silicotungstic acid, a silicomolybdic acid and the like.

The hydrocarbyl-substituted carboxylic acid acylating agents may be made by reacting one or more alpha-beta olefinically unsaturated carboxylic
25 acid reagents containing 2 to about 20 carbon atoms, exclusive of the carboxyl groups, with one or more olefin polymers as described more fully hereinafter. This reaction may occur under the conditions to add the alpha-beta olefinically unsaturated carboxylic acid reagents via a free radical addition process.

30 In one embodiment, the hydrocarbyl-substituted carboxylic acid acylating agent is a polyisobutene-substituted succinic anhydride, the

polyisobutene substituent having a number average molecular weight of about 1,500 to about 3,000, in one embodiment about 1,800 to about 2,300, in one embodiment about 700 to about 1300, in one embodiment about 800 to about 1000, said first polyisobutene-substituted succinic anhydride being
5 characterized by about 1.3 to about 2.5, and in one embodiment about 1.7 to about 2.1 In one embodiment, the hydrocarbyl-substituted carboxylic acid acylating agent is a polyisobutene-substituted succinic anhydride, the polyisobutene substituent having a number average molecular weight of about 1,500 to about 3,000, and in one embodiment about 1,800 to about 2,300,
10 said first polyisobutene-substituted succinic anhydride being characterized by about 1.3 to about 2.5, and in one embodiment about 1.7 to about 2.1, in one embodiment about 1.0 to about 1.3, and in one embodiment about 1.0 to about 1.2 succinic groups per equivalent weight of the polyisobutene substituent.

15 The fuel-soluble product (i) may be formed using ammonia, an amine and/or the metal bases of metals such as Na, K, Ca, and the like. The amines useful for reacting with the acylating agent to form the product (i) including but are not limited to, monoamines, polyamines, alkanol amines, hydroxy amines, and mixtures thereof, and amines may be primary, secondary or tertiary
20 amines.

Examples of primary and secondary monoamines include ethylamine, diethylamine, n-butylamine, di-n-butylamine, allylamine, isobutylamine, cocoamine, stearylamine, laurylamine, methyl laurylamine, oleylamine, N-methyloctylamine, dodecylamine, and octadecylamine. Suitable examples of
25 tertiary monoamines include trimethylamine, triethylamine, tripropylamine, tributylamine, monoethyldimethylamine, dimethylpropylamine, dimethylbutylamine, dimethylpentylamine, dimethylhexylamine, dimethylheptylamine, and dimethyloctylamine.

The amines include but are not limited to hydroxyamines, such as
30 mono-, di-, and triethanolamine, dimethylethanol amine, diethylethanol amine, di-(3-hydroxy propyl) amine, N-(3-hydroxybutyl) amine, N-(4-hydroxy butyl) amine, and N,N-di-(2-hydroxypropyl) amine; alkylene polyamines such as

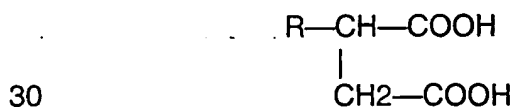
methylene polyamines, ethylene polyamines, butylene polyamines, propylene polyamines, pentylene polyamines, and the like. Specific examples of such polyamines include ethylene diamine, diethylene triamine, triethylene tetramine, propylene diamine, trimethylene diamine, tripropylene tetramine, 5 tetraethylene pentamine, hexaethylene heptamine, pentaethylene hexamine, or a mixture of two or more thereof; ethylene polyamine bottoms or a heavy polyamine. The fuel-soluble product (i) may be a salt, an ester, an ester/salt, an amide, an amide, or a combination of two or more thereof.

The fuel-soluble product (i) may be present in the water fuel emulsion 10 at a concentration of up to about 15% by weight based on the overall weight of the emulsion, and in one embodiment about 0.1 to about 15% by weight, and in one embodiment about 0.1 to about 10% by weight, and in one embodiment about 0.1 to about 5% by weight, and in one embodiment about 0.1 to about 2% by weight, and in one embodiment about 0.1 to about 1% by 15 weight, and in one embodiment about 0.1 to about 0.7% by weight.

The second acylating agent (ii) of this invention includes carboxylic acids and their reactive equivalents such as acid halides and anhydrides.

In one embodiment, the carboxylic acid is a monocarboxylic acid of about 1 to about 35 carbon atoms, and in one embodiment about 16 to about 20 24 carbon atoms. Examples of these monocarboxylic acids include lauric acid, oleic acid, isostearic acid, palmitic acid, stearic acid, linoleic acid, arachidic acid, gadoleic acid, behenic acid, erucic acid, tall oil fatty acids, lignoceric acid and the like. These acids may be saturated, unsaturated, or have other functional groups, such as hydroxy groups, as in 12-hydroxy 25 stearic acid, from the hydrocarbyl backbone.

In one embodiment, the carboxylic acid is a hydrocarbyl-substituted succinic acid represented correspondingly by the formula



wherein formula R is hydrocarbyl group of about 12 to about 35, and in one embodiment from about 12 to about 30, and in one embodiment from about

16 to about 24 and in one embodiment from about 26 to about 35 carbon atoms. The production of such hydrocarbyl-substituted succinic acids or anhydrides via alkylation of maleic acid or anhydride or its derivatives with a halohydrocarbon or via reaction of maleic acid or anhydride with an olefin polymer having a terminal double bond is known to those of skill in the art.

In one embodiment, the acylating agent (ii) is a carboxylic acid or the acylating agent (ii) used to prepare carboxylic acid and is made by reacting one or more alpha-beta olefinically unsaturated carboxylic acid reagents containing about 2 to about 20 carbon atoms, exclusive of the carboxyl based groups, with one or more olefin polymers containing at least about 16 carbon atoms.

In the one embodiment, the ratio of the first acylating agent (i), to the second acylating agent (ii) in the emulsified fuel is in the range of about 9:1 to about 1:9; in another embodiment in the range of about 5:1 to about 1:5; and in another embodiment in the range of about 1:3 to about 3:1.

The ionic or nonionic compound (iii) of the emulsifier has a hydrophilic-lipophilic balance (HLB, which refers to the size and strength of the polar (hydrophilic) and non-polar (lipophilic) groups on the surfactant molecule) in the range of about 1 to about 40, and in one embodiment about 4 to about 15 and is described in greater detail in USSN 09/761,482, An Emulsifier For An Aqueous Hydrocarbon Fuel, incorporated by reference herein. Examples of these compounds are disclosed in McCutcheon's Emulsifiers and Detergents, 1998, North American & International Edition. Pages 1-235 of the North American Edition and pages 1-199 of the International Edition are incorporated herein by reference for their disclosure of such ionic and nonionic compounds having an HLB in the range of about 1 to about 40, in one embodiment about 1 to about 30, in one embodiment about 1 to 20, and in another embodiment about 1 to about 10. Examples include low molecular weight variants of (i) or (vii) such as those having a hydrocarbon group in the range of C₈ or C₂₀. Useful compounds include alkanolamines, carboxylates including amine salts, metallic salts and the like, alkylarylsulfonates, amine oxides, poly(oxyalkylene) compounds, including block copolymers comprising

alkylene oxide repeat units, carboxylated alcohol ethoxylates, ethoxylated alcohols, ethoxylated alkylphenols, ethoxylated amines and amides, ethoxylated fatty acids, ethoxylated fatty esters and oils, fatty esters, fatty acid amides, including but not limited to amides from tall oil fatty acids and
5 polyamides, glycerol esters, glycol esters, sorbitan esters, imidazoline derivatives, lecithin and derivatives, lignin and derivatives, monoglycerides and derivatives, olefin sulfonates, phosphate esters and derivatives, propoxylated and ethoxylated fatty acids or alcohols or alkylphenols, sorbitan derivatives, sucrose esters and derivatives, sulfates or alcohols or ethoxylated
10 alcohols or fatty esters, sulfonates of dodecyl and tridecyl benzenes or condensed naphthalenes or petroleum, sulfosuccinates and derivatives, and tridecyl and dodecyl benzene sulfonic acids.

The emulsifier (iv) may be a mixture of (i) and (ii) described above and is further described in detail in USSN 09/761,482, An Emulsifier For An
15 Aqueous Hydrocarbon Fuel, incorporated by reference herein.

The emulsifier of the water-soluble compound (v) may be an amine salt, ammonium salt, azide compound, nitro compound, nitrate salts, alkali metal salt, alkaline earth metal salt, or mixtures of two or more thereof and is described in greater detail in USSN 09/761,482, An Emulsifier For An
20 Aqueous Hydrocarbon Fuel, incorporated by reference herein. These compounds are distinct from the fuel-soluble product (i) and the ionic or nonionic compound (ii) discussed above. These water-soluble compounds include organic amine nitrates, nitrate esters, azides, nitramines and nitro compounds. Also included are alkali and alkaline earth metal carbonates,
25 sulfates, sulfides, sulfonates, and the like. In another embodiment the water soluble compound is in the form of a salt, such as an amine salt, ammonia salt, azide salt, alkali metal salt, alkaline earth metal salt, nitrate salt and mixtures thereof.

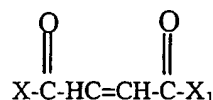
Particularly useful are the amine or ammonium salts such as
30 ammonium nitrate, ammonium acetate, methylammonium nitrate, methylammonium acetate, hydroxy ammonium nitrate, ethylene diamine diacetate; urea nitrate; urea; guanidinium nitrate; and combinations thereof.

However, these ammonium salts of the emulsifier, if used are independent of and distinct and separate from the aqueous organic ammonium salt compound of the emulsified fuel discussed above.

In one embodiment the emulsifier (vi) is the reaction product of A) a polyacidic polymer, B) at least one fuel soluble product made by reacting at least one hydrocarbyl-substituted carboxylic acid acylating agent, and C) a hydroxy amine and/or a polyamine and is described in greater detail in USSN 09/761,482, An Emulsifier For An Aqueous Hydrocarbon Fuel, incorporated by reference herein.

The polyacidic polymers used in the reaction include but are not limited to C₄ to C₃₀; preferably C₈ to C₂₀ olefin/maleic anhydride copolymers; maleic anhydride/styrene copolymers; poly-maleic anhydride; acrylic and methacrylic acid containing polymers; poly-(alkyl)acrylates; reaction products of maleic anhydride with polymers with multiple double bonds;

A copolymer of an olefin and a monomer having the structure:



wherein X and X₁ are the same or different provided that at least one of X and X₁ is such that the copolymer can function as a carboxylic acylating agent; and combinations therein.

The emulsifier produced from the reaction product of the polyacidic polymer with the fuel soluble product (i) comprises about 25% to about 95% of fuel soluble product and about 0.1% to about 50% of the polyacidic polymer; preferably about 50% to about 92% fuel soluble product and about 1% to about 20% of the polyacidic polymer, and most preferably about 70% to about 90% of fuel soluble product and about 5% to about 10% of the polyacidic polymer. In one embodiment the emulsifier is described as a polyalkenyl succinimide crosslinked with an olefin/maleic anhydride copolymer.

The amino alkyl emulsifier (vii) is comprised of the reaction product of an amino alkylphenol, an aldehyde, and an amine resulting in amino

alkylphenol. The amino alkylphenol can be made by (a) the reaction of alkylphenol directly with an aldehyde and an amine resulting in an alkylphenol monomer connected by a methylene group to an amine, (b) the reaction of an alkylphenol with an aldehyde resulting in an oligomer wherein the alkylphenols are bridged with methylene groups, the oligomer is then reacted with more aldehyde and an amine to give a Mannich product, or (c) a mixture of (a) and (b) and is described in greater detail in USSN 09/977,747 entitled A Continuous Process For Making An Aqueous Hydrocarbon Fuel Emulsion incorporated by reference herein.

The alkylphenols have an alkyl group selected from C_1 to C_{200} , preferably C_6 to C_{170} wherein the alkyl group is either linear, branched or a combination thereof. The alkylphenols include, but are not limited to, polypropylphenol, polybutylphenol, poly(isobutenyl)phenol, polyamylphenol, tetrapropylphenol, similarly substituted phenols and the like. The preferred alkylphenols are tetrapropenylphenol and poly(isobutenyl)phenol.

The aldehydes include, but are not limited to, aliphatic aldehydes, such as formaldehyde; acetaldehyde; aldol (β -hydroxy butyraldehyde); aromatic aldehydes, such as benzaldehyde; heterocyclic aldehydes, such as furfural, and the like. The aldehyde may contain a substituent group such as hydroxyl, halogen, nitro and the like; in which the substituent does not take a major part in the reaction. The preferred aldehyde is formaldehyde.

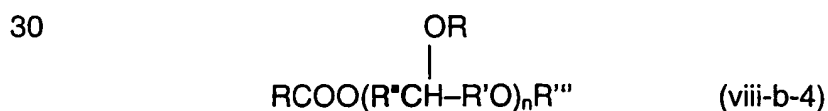
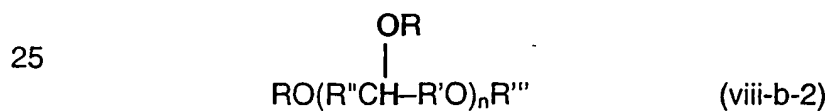
The amines are those which contain an amino group characterized by the presence of at least one active hydrogen atom. The amines may be primary amino groups, secondary amino groups, or combinations of primary and secondary amino groups.

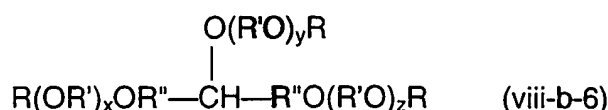
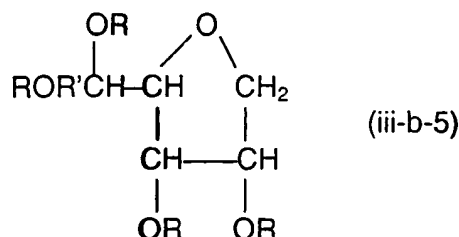
The amines include, but are not limited to, alkanolamines; di- and polyamine (polyalkylene amines); polyalkyl polyamines; propylenediamine, the aromatic amines such as o-, m- and p-phenylene diamine, diamino naphthalenes; the acid-substituted polyalkylpolyamines, and the corresponding formyl-, propionyl-, butyryl-, and the like N-substituted compounds; and the corresponding cyclized compounds formed therefrom, such as the N-alkyl amines of imidazolidine and pyrimidine. Substituent

groups attached to the carbon atoms of these amines are typified by alkyl, aryl, alkaryl, aralkyl, cycloalkyl, and amino compounds. The amino alkylphenols emulsifier of this invention may be made by reacting the alkylphenol:aldehyde:amine in a ratio range of 1:1:0.1 molar to 1:2:2 molar, in one embodiment preferably 1:0.9:0.1 to 1:1.9:1.9, in one embodiment preferably 1:1.5:1.2 molar to 1:1.9:1.8 molar, and in one embodiment preferably 1:0.8:0.3 to 1:1.5:0.7, resulting in the amino alkylphenol emulsifier. In another embodiment of this invention the amino alkylphenol is made by the reaction of an alkylphenol with an aldehyde, resulting in an oligomer wherein the alkylphenols are bridged with methylene groups; then the oligomer is reacted with more aldehyde and amine to give the emulsifier Mannich product of this invention. The reaction is prepared by any known method such as an emulsion, a solution, a suspension, and a continuous addition bulk process. The reaction is carried out under conditions that provide for the formation of the desired product.

The nitrogen-free emulsifier (viii) comprises:

- (viii)(a) a hydrocarbyl substituted carboxylic acid, or a reaction product of the hydrocarbyl substituted carboxylic acid or a reactive equivalent of such acid with an alcohol, the hydrocarbyl substituent of the acid or reactive equivalent thereof containing at least about 30 carbon atoms; and
- (viii)(b) at least one compound represented by one or more of the formulae:





wherein each R is independently hydrogen or a hydrocarbyl group of up to about 60 carbon atoms; each R' and R'' is independently an alkylene group of 1 to about 20 carbon atoms; each R''' is independently hydrogen, or an acyl or hydrocarbyl group of up to about 30 carbon atoms; n is a number in the range of zero to about 50; and x, y and z are independently numbers in the range of zero to about 50 with the total for x, y and z being at least 1. This emulsifier is further disclosed in Applicants U.S. application entitled "Water Blended Fuel Composition", Applicants' reference number 3134, USSN_____, incorporated by reference herein.

The emulsifier component (viii) (a) may be a hydrocarbyl substituted carboxylic acid, or a reaction product of the hydrocarbyl substituted carboxylic acid or a reactive equivalent thereof with an alcohol. The carboxylic acids may be monobasic or polybasic. The polybasic acids include dicarboxylic acids, although tricarboxylic and tetracarboxylic acids may be used. The reactive equivalents may be acid halides, (e.g., chlorides), anhydrides or esters, including partial esters, and the like.

The alcohol which may be reacted with the hydrocarbyl substituted carboxylic acid or reactive equivalent to form emulsifier component (iii)(a) may be a mono- or polyhydric hydrocarbon-based alcohol such as methanol, ethanol, the propanols, butanols, pentanols, hexanols, heptanols, octanols, decanols, and the like. Also included are fatty alcohols and mixtures thereof, including saturated alcohols such as lauryl, myristyl, cetyl, stearyl and behenyl alcohols, and unsaturated alcohols such as palmitoleyl, oleyl and eicosenyl.

Higher synthetic monohydric alcohols of the type formed by the Oxo process (e.g., 2-ethylhexanol), by the aldol condensation, or by organoaluminum-catalyzed oligomerization of alpha-olefins (e.g., ethylene), followed by oxidation, may be used. Alicyclic analogs of the above-described alcohols
5 may be used; examples include cyclopentanol, cyclohexanol, cyclododecanol, and the like.

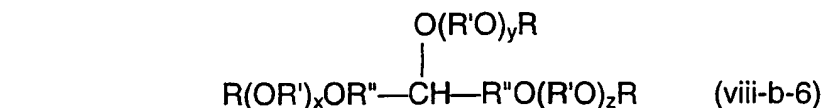
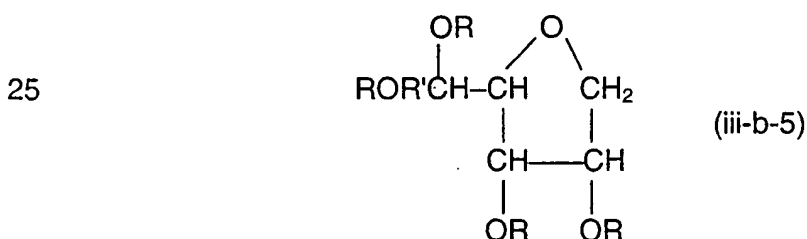
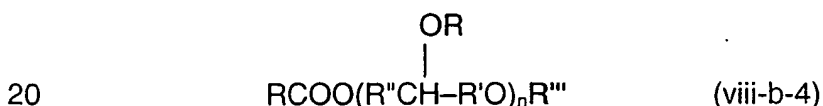
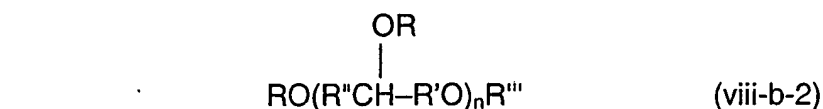
The polyhydroxy compounds that may be used include ethylene, propylene, butylene, pentylene, hexylene and heptylene glycols; tri-, tetra-, penta-, hexa- and heptamethylene glycols and hydrocarbon-substituted
10 analogs thereof (e.g., 2-ethyl-1,3-trimethylene glycol, neopentyl glycol, etc.), as well as polyoxyalkylene compounds such as diethylene and higher polyethylene glycols, tripropylene glycol, dibutylene glycol, dipentylene glycol, dihexylene glycol and diheptylene glycol, and their monoethers. A glycol that may be used is 1,2-propane diol.

15 Phenol, naphthols, substituted phenols (e.g., the cresols), and dihydroxyaromatic compounds (e.g., resorcinol, hydroquinone), as well as a benzyl alcohol and similar di-hydroxy compounds wherein the second hydroxy group is directly bonded to an aromatic carbon (e.g., 3-HO Φ CH₂OH wherein Φ is a divalent benzene ring) may be used. Sugar alcohols of the general
20 formula HOCH₂ (CHOH)₁₋₅ CH₂OH such as glycerol, sorbitol, mannitol, and the like, and their partially esterified derivatives may be used. Oligomers of such sugar alcohols, including diglycerol, triglycerol, hexaglycerol, and the like, and their partially esterified derivatives may be used. Methylol polyols such as pentaerythritol and its oligomers (di- and tripentaerythritol, etc.),
25 trimethylolethane, trimethylolpropane, and the like may be used.

The emulsifier component (viii)(a) may be in the form of an acid, an ester, or a mixture thereof. The acid may be formed by reacting a hydrocarbyl substituted carboxylic acid reactive equivalent with water to provide the desired acid. For example, hydrocarbyl (e.g., polyisobutene)
30 substituted succinic anhydride may be reacted with water to form hydrocarbyl substituted succinic acid. The reaction between the hydrocarbyl substituted carboxylic acid or reactive equivalent thereof and the alcohol to form an ester

may be carried out under suitable ester forming reaction conditions. In one embodiment, the hydrocarbyl substituted carboxylic acid or reactive equivalent thereof and the alcohol are reacted in amounts sufficient to provide from about 0.3 to about 3 equivalents of the acid or reactive equivalent thereof per equivalent of alcohol. In one embodiment, this ratio is from about 0.5:1 to about 2:1.

The emulsifier component (viii)(b) may be at least one compound represented by one or more of the formulae:



35

wherein each R is independently hydrogen or a hydrocarbyl group of up to about 60 carbon atoms; each R' and R'' is independently an alkylene group of 1 to about 20 carbon atoms; each R''' is independently hydrogen, or

an acyl or hydrocarbyl group of up to about 30 carbon atoms; n is a number in the range of zero to about 50; and x, y and z are independently numbers in the range of zero to about 50 with the total for x, y and z being at least 1. In the above formulae, R may be a hydrocarbyl group of about 6 to about 60 carbon atoms, and in one embodiment about 6 to about 45 carbon atoms, and in one embodiment about 6 to about 30 carbon atoms, and in one embodiment about 14 to about 30 carbon atoms. In one embodiment, R may be a hydrocarbyl group of about 9 to about 11 carbon atoms. R' and R'' may be independently alkylene groups of about 1 to about 6 carbon atoms, and in one embodiment about 1 to about 4 carbon atoms. In one embodiment, R' is an alkylene group containing about 2 to about 3 carbon atoms, and in one embodiment about 2 carbon atoms. In one embodiment, R'' is an alkylene group containing 1 carbon atom. R''' may be an acyl or hydrocarbyl group of 1 to about 30 carbon atoms, and in one embodiment 1 to about 24 carbon atoms, and in one embodiment 1 to about 18 carbon atoms, and in one embodiment 1 to about 12 carbon atoms, and in one embodiment 1 to about 6 carbon atoms. n may be a number in the range of 1 to about 50, and in one embodiment 1 to about 30, and in one embodiment 1 to about 20, and in one embodiment 1 to about 12, and in one embodiment about 4 to about 10, and in one embodiment about 5 to about 10, and in one embodiment about 5 to about 8, and in one embodiment about 5 or about 6. x, y and z may be independently numbers in the range of zero to about 50, and in one embodiment zero to about 30, and in one embodiment zero to about 10; with the total of x, y and z being at least 1, and in one embodiment in the range of 1 to about 50, and in one embodiment 10 to about 40, and in one embodiment 20 to about 30, and in one embodiment about 25.

Examples of compounds represented by formula (viii-b-1) that may be used include: C₉-C₁₁ alkoxy poly (ethoxy)₈ alcohol; C₁₂-C₁₅ alkoxy poly (isopropoxy)₂₂₋₂₆ alcohol; oleyl alcohol pentaethoxylate; and the like.

Examples of compounds represented by formula (viii-b-2) that may be used include diglycerol monooleate, diglycerol monostearate, polyglycerol monooleate, and the like.

5 Examples of compounds represented by formula (viii-b-4) that may be used include glycerol monooleate, diglycerol dioleate, diglycerol distearate, polyglycerol dioleate, and the like.

Examples of compounds represented by formula (viii-b-5) that may be used include sorbitan monooleate, sorbitan monoisostearate, sorbitan sesquioleate, and sorbitan trioleate, and the like.

Examples of compounds represented by formula (viii-b-6) that may be used include polyethoxy glycerol trioleate wherein the compound contains 25 ethoxy groups.

In one embodiment, the emulsifier (viii)(b) is an alkoxy polyethoxy alcohol wherein the alkoxy group contains about 14 to about 30 carbon atoms and the polyethoxy group contains up to about 10 ethoxy groups, and in one embodiment about 5 to about 10 ethoxy groups, and in one embodiment about 5 or 6 ethoxy groups.

In one embodiment, the emulsifier (viii)(b) is an alkoxy polyethoxy alcohol wherein the alkoxy group contains about 9 to about 11 carbon atoms and the polyethoxy group contains about 8 ethoxy groups.

An optional acid component that may be used in one embodiment with the nitrogen free emulsifier and in another embodiment with each of the emulsifiers alone or in combinations may be used in the inventive fuel composition comprises one or more acids having a pKa of up to about 6, and in one embodiment up to about 5, and in one embodiment up to about 4, and in one embodiment from about 0 to about 4, and in one embodiment about 1 to about 3.5, and in one embodiment about 1.5 to about 3. This acid component includes but is not limited too carboxylic acid, formic acid, acetylenedicarboxylic acid, benzenehexacarboxylic acid, benzenepentacarboxylic acid, benzenetetracarboxylic acid, benzenetricarboxylic acid, 2-butyne-1,4-dioic acid, 2-butyneic acid, citraconic acid, cyclopropane-1,1-

dicarboxylic acid, 2,6-dihydroxybenzoic acid, dihydroxymaleic acid, dihydroxymalic acid, dihydroxytartaric acid, alpha, alpha-dimethyloxaloacetic acid, dipropylmalonic acid, ethylene oxide dicarboxylic acid, hydroxyaspartic acid, maleic acid, 2-oxobutanoic acid, triethylsuccinic acid, citric acid, tartaric acid, glyoxylic acid, oxalic acid, lactic acid, oxomalonic acid (mesoxalic acid), and mixtures thereof.

When used, this acid component may function as an ionizing agent. The concentration of this acid component in the water blended fuel composition may range up to about 5 percent by weight, and in one embodiment from about 0.001 to about 3 percent by weight, and in one embodiment about 0.01 to about 1 percent by weight.

Other Additives

In one embodiment, the emulsified fuel contains a cetane improver. The cetane improvers that are useful include but are not limited to peroxides, nitrates, nitrites, nitrocarbarnates, and the like. Useful cetane improvers include but are not limited to nitropropane, dinitropropane, tetranitromethane, 2-nitro-2-methyl-1-butanol, 2-methyl-2-nitro-1-propanol, and the like. Also included are nitrate esters of substituted or unsubstituted aliphatic or cycloaliphatic alcohols which may be monohydric or polyhydric. These include substituted and unsubstituted alkyl or cycloalkyl nitrates having up to about 10 carbon atoms, and in one embodiment about 2 to about 10 carbon atoms. The alkyl group may be either linear or branched, or a mixture of linear or branched alkyl groups. Examples include methyl nitrate, ethyl nitrate, n-propyl nitrate, isopropyl nitrate, allyl nitrate, n-butyl nitrate, isobutyl nitrate, sec-butyl nitrate, isooctyl nitrate, tert-butyl nitrate, n-amyl nitrate, isoamyl nitrate, 2-amyl nitrate, 3-amyl nitrate, tert-amyl nitrate, n-hexyl nitrate, n-heptyl nitrate, n-octyl nitrate, 2-ethylhexyl nitrate, sec-octyl nitrate, n-nonyl nitrate, n-decyl nitrate, cyclopentyl nitrate, cyclohexyl nitrate, methylcyclohexyl nitrate, and isopropylcyclohexyl nitrate. Also useful are the nitrate esters of alkoxy-substituted aliphatic alcohols such as 2-ethoxyethyl nitrate, 2-(2-ethoxy-ethoxy) ethyl nitrate, 1-methoxypropyl-2-nitrate, 4-ethoxybutyl nitrate,

etc., as well as diol nitrates such as 1,6-hexamethylene dinitrate. A useful cetane improver is 2-ethylhexyl nitrate.

The concentration of the cetane improver in the emulsified fuel is at any concentration sufficient to provide the emulsion with the desired cetane number. In one embodiment, the concentration of the cetane improver is at a level of up to about 10% by weight, and in one embodiment about 0.05% to about 10% by weight, and in one embodiment about 0.05% to about 5% by weight, and in one embodiment about 0.05% to about 1% by weight of the emulsified fuel.

In addition to the foregoing materials, other fuel additives that known to those skilled in the art may be used in the emulsified fuel. These include but are not limited to dyes, rust inhibitors such as alkylated succinic acids and anhydrides, bacteriostatic agents, gum inhibitors, metal deactivators, upper cylinder lubricants and the like.

The total concentration of the additives, in the emulsified fuel is from about 0.05% to about 30% by weight, and in one embodiment about 0.1% to about 20% by weight, and in one embodiment about 0.1% to about 15% by weight, and in one embodiment about 0.1% to about 10% by weight, and in one embodiment about 0.1% to about 5% by weight of the emulsified fuel.

The additives, including the foregoing emulsifiers, may be diluted with a substantially inert, normally liquid organic solvent such as naphtha, benzene, toluene, xylene or diesel fuel to form an additive concentrate which is then mixed with the fuel and water to form the emulsified fuel.

The emulsified fuel may contain up to about 60% by weight organic solvent, and in one embodiment about 0.01% to about 50% by weight, and in one embodiment about 0.01% to about 20% by weight, and in one embodiment about 0.1% to about 5% by weight, and in one embodiment about 0.1% to about 3% by weight of the emulsified fuel.

The emulsified fuel may additionally contain an antifreeze agent. The antifreeze agent is typically an alcohol. Examples include but are not limited to ethylene glycol, propylene glycol, methanol, ethanol, glycerol and mixtures of two or more thereof. The antifreeze agent is typically used at a

concentration sufficient to prevent freezing of the water used in the water fuel emulsion. The concentration is therefore dependent upon the temperature at which the fuel is stored or used. In one embodiment, the concentration is at a level of up to about 20% by weight of the emulsified fuel, and in one
5 embodiment about 0.1% to about 20% by weight, and in one embodiment about 1% to about 10% by weight of the emulsified fuel.

Engines

The engines that may be operated in accordance with the invention include all (internal combustion) engines including spark ignited (gasoline)
10 and compression ignited (diesel) for both mobile including locomotive, marine, automotive, truck, heavy duty, aviation and the like, and stationary power plants. The engines may be two-cycle or four-cycle. The engines may employ conventional after treatment devices. Included are on- and off-highway engines, including new engines as well as in-use engines.

15 An open-flame burning apparatus may be operated with the emulsified water fuel blend of the invention. The open-flame burning apparatus may be any open-flame burning apparatus equipped to burn a liquid fuel. These include domestic, commercial and industrial burners. The industrial burners include those requiring preheating for proper handling and atomization of the
20 fuel. Also included are oil fired combustion units, oil fired power plants, fired heaters and boilers, and boilers for use in ships including deep draft vessels. The fuel burning apparatus may be a boiler for commercial applications included are boilers for power plants, utility plants, and large stationary and marine engines. The open-flame fuel burning apparatus may be an
25 incinerator or a rotary kiln incinerator, liquid injection kiln, fluidized bed kiln, cement kiln, and the like. Also included are steel and aluminium forging furnaces. The open-flame burning apparatus may be equipped with a flue gas recirculation system.

From the above description and examples the invention those skilled in
30 the art may perceive improvements, changes and modifications in the invention. Such improvement changes and modifications are intended to be covered by the appended claims.

What is Claimed:

1. An emulsified water in oil composition comprising:
 - 5 A) a fuel;
 - B) a water;
 - C) a high molecular weight emulsifier;
 - D) a surfactant having a molecular weight of about less than or equal to about 950 g/mol wherein the surfactant comprises:
 - 10 i) natural fats;
 - ii) non-ionic and ionic surfactants;
 - iii) co-surfactants;
 - iv) fatty acids and their amine salts; or
 - v) combinations thereof; and
 - 15 E) optionally ammonium nitrate.
2. The composition of claim 1 wherein a fuel is in the range of about 50% to about 99% by weight of the composition; the water is in the range of about 1% to about 50% by weight of the composition; the emulsifier is in the range of about 1% to about 50% by weight of the composition; and the
20 surfactant in the range of about 0.001% to about 15% by weight of the composition.
3. The composition of claim 1 wherein a fuel is in the range of about 50% to about 99% by weight of the composition; the water is in the range of less than 1% by weight of the composition; the emulsifier is in the range of
25 about 1% to about 50% by weight of the composition; and the surfactant in the range of about 0.001% to about 15% by weight of the composition.
4. The composition of claim 1 wherein the fuel is a diesel fuel.
5. The composition of claim 1 wherein the water in oil composition is an emulsified water blended fuel and wherein the fuel is selected from the
30 group consisting of petroleum distillate fuel such as diesel, gasoline, fuel oil a mixture thereof; a fuel derived from vegetables, corn, alfalfa, rapeseed, soybeans, shale, coal or mixtures thereof; a biodegradable fuel; biodiesel;

residual fuel; bitumen; alcohol; ether; ethanol; Fischer-Tropsch fuels; and combinations thereof.

6. The composition of claim 1 wherein the surfactant has a low molecular weight in the range of about 900 g/mol to about 30 g/mol.

5 7. The composition of claim 1 wherein the surfactant has a low molecular weight in the range of about 400 g/mol to about 90 g/mol.

8. The composition of claim 1 wherein the surfactant is in the range of about 0.01% to about 10% by weight of the water in oil composition.

9. The composition of claim 1 wherein the natural fat surfactant is
10 selected from the group consisting of triglycerides, hydrolyzed triglycerides, oxidized products of triglycerides, vegetable oils, refined vegetable oils, used vegetable oils and combinations thereof.

10. The composition of claim 1 wherein the non ionic and ionic
15 surfactants are selected from the group consisting of alkyl ethoxylates, ethoxylated alkylphenols, alkyl glucosides, ethoxylated alcohols, ethoxylated amines, ethoxylated amides derived from fatty acids, amides derived from fatty alcohols, ethers alcohols, fatty alcohols, esters of fatty acids ethers of fatty acids, esters of fatty alcohols and combinations thereof.

11. The composition of claim 1 wherein the non-ionic and ionic
20 surfactants have a hydrophilic lipophilic balance (HLB) in the range of about 2 to about 40.

12. The composition of claim 11 wherein the non-ionic and ionic
surfactants are selected from the group consisting of alkanolamides,
alkylarylsulfonates, amine oxides, poly(oxyalkylene) compounds, including
25 block copolymers comprising alkylene oxide repeat units (Pluronic™), carboxylated alcohol ethoxylates, such as fatty esters, glycerol esters, glycol esters, imidazoline derivatives, lecithin and derivatives, lignin and derivatives, monoglycerides and diglycerides and derivatives, phosphate esters and derivatives, propoxylated fatty acids, propoxylated fatty alcohols, alkyl
30 phenols, sorbitan derivatives, sucrose esters, derivatives of sucrose esters, sulfates or alcohols or ethoxylated alcohols or fatty esters, sulfonates of

dodecyl aoxtridecyl benzenes or condensed naphthalenes, and combinations thereof.

13. The composition of claim 8 wherein the non-ionic and ionic surfactants are selected from the group consisting of C12 – C 14 alcohol with two ethoxylates, ethomeen C12, Neodol 25-3, oleylic alcohol with 5 ethoxylates, (nonylphenoxypoly(ethyleneoxy) ethanol, nonoxynol-8), (a-(4-nonylphenyl)- ∞ -hydroxypoly(oxy-1,2-ethanediyl)), alcohol ethoxylates, sorbitan monooleate, sorbitan monoisostearate , glycerol dioleate, glycerol monooleate, lauric acid, myristic acid, coconut acid, coconut oil, oleic acid, tall oil fatty acid, linoleic acid, soybean oil, apricot kernel oil, wheat germ oil, monocarboxylic fatty acids, triglycerides, and combinations thereof.

14. The composition of claim 1 wherein the co-surfactant is selected from the group consisting of alcohols, amines, amides, ketones, esters, ethers and combinations thereof and further wherein the co-surfactant has from about 1 to about 24 carbon atoms.

15. The composition of claim 14 wherein the alcohols are selected from the group consisting of propylene glycol, ethylene glycol, isopropanol, 2 ethyl hexanol, stearyl alcohol, oleyl alcohol methanol, ethanol and combinations thereof.

16. The composition of claim 1 wherein the fatty acids and their amine salt surfactants are selected from the group consisting of diethyl ethanolamine salts of oleic acid, tall oil fatty acids, stearic acid, palmitic acid, lauric acid and combinations thereof.

17. A process for making a water in oil composition comprising shearing;

A) a fuel in the range of about 50% to about 99% by weight of the composition;

B) a water in the range of about 1% to 50% by weight of the composition;

C) a high molecular weight emulsifier in the range of about 1% to about 50% by weight of the composition;

D) a low molecular weight surfactants in the range of about 0.001% to about 15% by weight of the composition wherein the surfactant comprises natural fats, non ionic surfactants, co-surfactant having about 1 to 24 carbon atoms; fatty acids and their amine salts; and combinations thereof
5 and wherein the shearing mixing occurs at a shear rate in the range of less than or equal to $50,000 \text{ s}^{-1}$; and

E) optionally ammonium nitrate.

18. The process of claim 17 wherein the shear rate in the range of about $20,000 \text{ s}^{-1}$ to about 1 s^{-1} .

10 19. The process of claim 17 wherein the shear rate is in the range of about $1,000 \text{ s}^{-1}$ to about 1 s^{-1} .

20. The process of claim 17 wherein the water in oil composition is an emulsified water in fuel and wherein the fuel is selected from the group consisting of petroleum distillate fuel such as diesel, gasoline, fuel oil a
15 mixture thereof, a fuel derived from vegetables, corn, alfalfa, rapeseed, soybeans, shale, coal or mixtures thereof, a biodegradable fuel, biodiesel, residual fuel, bitumen, alcohol, ether, ethanol and combinations thereof..

21. The composition of claim 1 wherein the emulsifier is selected from the group consisting of

20 A) at least one fuel-soluble product made by reacting at least one hydrocarbyl-substituted carboxylic acid acylating agent with ammonia or an amine including but not limited to alkanol amine, hydroxy amine, and the like, the hydrocarbyl substituent of said acylating agent having about 50 to about 500 carbon atoms;

25 B) a second acylating agent having at least one hydrocarbyl substituents of up to about 40 carbon atoms, and reacting that said acylating agent with ammonia or an amine;

C) a water-soluble compound selected from the group consisting of amine salts, ammonium salts, azide salt, nitrate ester salt, alkali metal salts,
30 alkaline earth metal salts or mixtures thereof in combination with A, B, D, E, F or G;

D) the reaction product of polyacidic polymer with at least one fuel soluble product made by reacting at least one hydrocarbyl-substituted carboxylic acid acylating agent with ammonia, an amine, a polyamine, an alkanol amine or hydroxy amines;

5 E) an amino alkylphenol which is made by reacting an alkylphenol, an aldehyde and an amine resulting in an amino alkylphenol;

F) nitrogen free emulsifier; or

G) the combination of (A), (B), (C), (D), (E), (F) or combinations thereof.

10 22. The composition claim 1 wherein the water in oil composition is an emulsified fuel used to operate an apparatus selected from the group consisting of an engine, an open flame burner, and an internal combustion engines.

23. A process for making a water in oil composition comprising
15 shearing;

A) a fuel in the range of about 50% to about 99% by weight of the composition;

B) a water in the range of less than about 1% by weight of the composition;

20 C) a high molecular weight emulsifier in the range of about 1% to about 50% by weight of the composition;

D) a low molecular weight surfactants in the range of about 0.001% to about 15% by weight of the composition wherein the surfactant comprises natural fats, non ionic surfactants, co-surfactant having about 1 to 24 carbon
25 atoms; fatty acids and their amine salts; and combinations thereof and wherein the shearing mixing occurs at a shear rate in the range of less than or equal to $50,000 \text{ s}^{-1}$; and

E) optionally ammonium nitrate.

24. The process of claim 23 wherein the water is in the range of about
30 0.01% to about 1% by weight of the composition.

25. A process for making a water in oil composition comprising shearing;

A) a fuel in the range of about 50% to about 99% by weight of the composition;

B) a water in the range of less than about 1% by weight of the composition;

5 C) a high molecular weight emulsifier in the range of about 1% to about 50% by weight of the composition; and

D) a low molecular weight surfactants in the range of about 0.001% to about 15% by weight of the composition wherein the surfactant comprises natural fats, non ionic surfactants, co-surfactant having about 1 to 24 carbon atoms; fatty acids and their amine salts; and combinations thereof and wherein the shearing mixing occurs at a shear rate in the range of less than or equal to $50,000 \text{ s}^{-1}$.

26. The process of claim 25 wherein the water is in the range of about 0.01% to about 1% by weight of the composition.

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tional Application No

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A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C10L1/32 C10L1/10 C10L1/02 C10L10/02 B01F17/00
B01F3/08

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C10L B01F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 02/061017 A (LUBRIZOL CORP) 8 August 2002 (2002-08-08) cited in the application the whole document -----	1,2, 4-15, 17-22
X	US 2002/116868 A1 (MULLAY JOHN J ET AL) 29 August 2002 (2002-08-29) cited in the application the whole document -----	1,2, 4-15, 17-22
X	WO 00/15740 A (LUBRIZOL CORP) 23 March 2000 (2000-03-23) page 7, paragraph 3; claims 1-48 ----- -/-	1,2,4-8, 10-15, 21,22

☒ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

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8 document member of the same patent family

Date of the actual completion of the international search

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INTERNATIONAL SEARCH REPORT

 International Application No
 PCT/US 03/40041

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 02/068334 A (DALY DANIEL T ; LUBRIZOL CORP (US); BAKER MARK R (US); WOLAK THOMAS J) 6 September 2002 (2002-09-06) the whole document	1,2, 4-15,21, 22
X	US 6 280 485 B1 (ABRAHAM WILLIAM D ET AL) 28 August 2001 (2001-08-28) cited in the application the whole document	1,2,4-8, 10-15, 21,22
X	WO 02/094889 A (SCHUERMANN GREGOR ; BASF AG (DE); MACH HELMUT (DE); HUEFFER STEPHAN (D) 28 November 2002 (2002-11-28) page 14 - page 15; claims 13,15,16; table 2	1,2,4-8, 10-15, 17,18, 20,21
X	WO 01/04239 A (LUBRIZOL CORP) 18 January 2001 (2001-01-18) cited in the application page 3, paragraph 1; claims 1-17; examples 4,5 page 41, line 17 - page 42, line 30 page 46, line 26 - line 34	1,2,4-8, 10-12, 14,15, 17,18, 20-22
X	US 3 876 391 A (ECKERT GEORGE W ET AL) 8 April 1975 (1975-04-08) column 5, line 1 - line 15 column 6, line 20 - line 25	1-8, 10-15, 17-26
X	US 5 693 106 A (PETER-HOBLYN JEREMY D ET AL) 2 December 1997 (1997-12-02) column 6 - column 8; claims 1-20	1-8, 10-12, 14,21,22
X	US 4 083 698 A (STEINMANN HENRY W ET AL) 11 April 1978 (1978-04-11) column 7, line 12 - line 23; claims 1-16	1-9, 13-15, 17-26
X	US 4 392 865 A (CHERRY NORMAN H ET AL) 12 July 1983 (1983-07-12) column 2, line 9 - line 12; claims 1-26 column 4, line 21 - line 48	1,2,4-8, 10-13, 17-22
X	US 4 162 143 A (YOUNT JOSEPH B) 24 July 1979 (1979-07-24) the whole document	1-8,11, 12,21,22

-/--

INTERNATIONAL SEARCH REPORT

tional Application No

PCT/US 03/40041

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4 744 797 A (SHIMADA YOSHINARI ET AL) 17 May 1988 (1988-05-17) the whole document -----	1,5-8, 11,13, 14,21,22

Form PCT/ISA/210 (continuation of second sheet) (January 2004)

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 03/40041

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
WO 02061017	A	08-08-2002	US 2001020344 A1	13-09-2001
			US 2001022046 A1	20-09-2001
			WO 02061017 A2	08-08-2002
			US 2002020106 A1	21-02-2002
			US 2002116868 A1	29-08-2002
US 2002116868	A1	29-08-2002	US 2002014033 A1	07-02-2002
			US 6383237 B1	07-05-2002
			US 6368367 B1	09-04-2002
			US 6368366 B1	09-04-2002
			US 2001022046 A1	20-09-2001
			US 2001020344 A1	13-09-2001
			BR 0116508 A	06-01-2004
			CA 2430955 A1	22-08-2002
			CN 1484687 T	24-03-2004
			EP 1358304 A2	05-11-2003
			WO 02064708 A2	22-08-2002
			AU 767781 B2	27-11-2003
			AU 5896100 A	30-01-2001
			BR 0012359 A	11-06-2002
			CA 2378505 A1	18-01-2001
			EP 1224248 A1	24-07-2002
			JP 2003504486 T	04-02-2003
			WO 0104239 A1	18-01-2001
			US 2002088167 A1	11-07-2002
			US 2001005955 A1	05-07-2001
			US 2002020106 A1	21-02-2002
			WO 02061017 A2	08-08-2002
WO 0015740	A	23-03-2000	US 6648929 B1	18-11-2003
			AU 756872 B2	23-01-2003
			AU 5812499 A	03-04-2000
			CA 2344044 A1	23-03-2000
			EP 1123365 A1	16-08-2001
			JP 2002525385 T	13-08-2002
			US 2002088167 A1	11-07-2002
			US 2002129541 A1	19-09-2002
			WO 0015740 A1	23-03-2000
WO 02068334	A	06-09-2002	US 6280485 B1	28-08-2001
			CA 2439470 A1	06-09-2002
			EP 1390454 A2	25-02-2004
			EP 1408788 A1	21-04-2004
			WO 02068570 A2	06-09-2002
			WO 02068334 A1	06-09-2002
US 6280485	B1	28-08-2001	WO 03020852 A2	13-03-2003
			US 6648929 B1	18-11-2003
			AU 756872 B2	23-01-2003
			AU 5812499 A	03-04-2000
			CA 2344044 A1	23-03-2000
			EP 1123365 A1	16-08-2001
			JP 2002525385 T	13-08-2002
			US 2002088167 A1	11-07-2002
			US 2002129541 A1	19-09-2002
			WO 0015740 A1	23-03-2000
WO 02094889	A	28-11-2002	DE 10125158 A1	05-12-2002

Form PCT/ISA/210 (patent family annex) (January 2004)

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 03/40041

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
WO 02094889	A		CA 2448033 A1	28-11-2002
			WO 02094889 A2	28-11-2002
			EP 1404726 A2	07-04-2004
WO 0104239	A	18-01-2001	US 6368366 B1	09-04-2002
			US 6368367 B1	09-04-2002
			US 6383237 B1	07-05-2002
			AU 767781 B2	27-11-2003
			AU 5896100 A	30-01-2001
			BR 0012359 A	11-06-2002
			CA 2378505 A1	18-01-2001
			EP 1224248 A1	24-07-2002
			JP 2003504486 T	04-02-2003
			WO 0104239 A1	18-01-2001
			US 2002088167 A1	11-07-2002
			US 2002014033 A1	07-02-2002
			US 2001005955 A1	05-07-2001
			US 2001020344 A1	13-09-2001
			US 2001022046 A1	20-09-2001
			US 2002020106 A1	21-02-2002
			US 2002116868 A1	29-08-2002
US 3876391	A	08-04-1975	NONE	
US 5693106	A	02-12-1997	US 5584894 A	17-12-1996
			BR 9606909 A	21-10-1997
			CA 2210256 A1	18-07-1996
			EP 0802960 A1	29-10-1997
			TW 390905 B	21-05-2000
			WO 9621708 A1	18-07-1996
			US 5501714 A	26-03-1996
			ZA 9600268 A	14-07-1997
			AU 2656495 A	21-12-1995
			CA 2191755 A1	07-12-1995
			EP 0763080 A1	19-03-1997
			WO 9533023 A1	07-12-1995
			US 5743922 A	28-04-1998
US 4083698	A	11-04-1978	DE 2653026 A1	24-05-1978
			US 4002435 A	11-01-1977
US 4392865	A	12-07-1983	AU 6781281 A	07-08-1981
			EP 0043843 A1	20-01-1982
			WO 8102024 A1	23-07-1981
			CA 1127845 A1	20-07-1982
			GB 1601174 A	28-10-1981
US 4162143	A	24-07-1979	AU 519833 B2	24-12-1981
			AU 4499979 A	20-09-1979
			CA 1122096 A1	20-04-1982
			DE 2963556 D1	14-10-1982
			EP 0004195 A2	19-09-1979
			JP 1052027 C	30-06-1981
			JP 54125206 A	28-09-1979
			JP 55042853 B	01-11-1980
US 4744797	A	17-05-1988	JP 1767500 C	11-06-1993
			JP 4050958 B	17-08-1992

Form PCT/ISA/210 (patent family annex) (January 2004)

INTERNATIONAL SEARCH REPORT

Additional Application No

PCT/US 03/40041

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 4744797	A	JP 60223896 A	08-11-1985
		AU 4235285 A	15-11-1985
		WO 8504895 A1	07-11-1985

Form PCT/ISA/210 (patent family annex) (January 2004)